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TITLE: THE MISUSED AND MISLEADING IAEA LEACH TEST

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AUTHOR(S): A. E. Ogard and E. A. Bryant

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THE MISUSED AND MISLEADING IAEA LEACH TEST*

A. E. Ogard and L. A. Bryant

Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545
U.S.A.

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ABSTRACT

Examples of data from IAEA leach tests on spent fuel elements are shown that were displayed, not in the recommended manner in the IAEA leach test, but in the manner of the modifications of this leach test. The main difference in the display methods is in the plotting of incremental leach rates as a function of cumulative time of leaching rather than as a function of the mean time of leaching of each individual sample. This difference in display can lead to wrong conclusions if the display methods are not carefully considered.

The leach test proposed by a panel of experts assembled by the IAEA in 1969 has been used in many laboratories studying the leaching of nuclear waste forms(1). In the simplest of terms this leach test is accomplished by placing a specified quantity of liquid in contact with a solid of a known surface area for a specified period of time, removing the liquid for analysis, and replacing the liquid with a fresh batch for the next time period. From the results of the analysis of the liquid one can calculate an incremental leach rate as follows:

$$R_n = \frac{a_n/A_o}{(F/V)t_n}$$

where a_n = radioactivity leached during the leachant renewal period, n.

A_o = radioactivity initially present in specimen.

F = exposed surface area of specimen (cm^2).

V = volume of specimen (cm^3).

t_n = duration (days) of leachant renewal period.

The results are in cm/day. Many scientists have changed this slightly so that the weight of the specimen is used rather than the volume. The results are then in the units of $g/cm^2/d$.

The IAEA leach test states that the incremental leach rate, R_n, should be plotted against $t = t_n - (t_n - t_{n-1})/2$; essentially the average time that the leachant and sample were in contact. It does not state that the incremental leach rate be plotted versus cumulated time, Σt_n.

A preliminary draft for an ISO-Standard for Long-Term Leach Testing of Radioactive Waste Solidification Products(2), on the other hand, plots the incremental leach rate, R_n, as a function of cumulative time(Σt)

of leaching. So called "modified IAEA" leach tests also plot R_n as a function of Σt.

The difference between plotting R_n as a function of $t = t_n - (t_n - t_{n-1})/2$ and Σt can be quite large. Figure 1 is an example of our results on spent fuel leaching in water(3). We have plotted the fraction leached per day of ^{154}Eu when leached from a spent fuel element under oxidizing and somewhat reducing conditions. The fraction leached per day, which is related to the incremental leach rate, was plotted versus the cumulated days of leaching in the manner of the ISO or modified IAEA leach test. Note the hump in the lower two curves found at ~7 to 8 days of leaching time. The explanation for the hump is quite simple. The IAEA sequence of sampling times was not followed and two short times (1 day each) at the 7th and 8th days followed a longer leach period. If the method of displaying data of the original IAEA test had been followed no hump would exist because all the 1 day samples would be grouped at 1 day on the abscissa, all 7 day samples would be grouped at 4 on the abscissa, etc. even though they were not taken in sequence, i.e. they would not be strung out in the sequence in which they were taken.

As defined, the IAEA and also the ISO-Standard leaching tests do not specifically point out the possibility that the rate of leaching, or dissolution, of a solid may be influenced by the changing composition of the leachant as the solid is dissolved. If there is such a feedback loop then one may expect the incremental leach rate to vary with the duration of the leach period. The composition of the leachant is "reset to zero" so to speak at the beginning of each new leach period. The longer the leach period the greater the change in leachant composition.

Thus, if the "feedback" is negative in sign a short leach period will exhibit a greater incremental leach rate than will a longer period. If the IAEA sampling requence is followed the result will be an apparant reducion in leach rate with time because of the constantly increasing leach periods. On the other hand if short and long leach periods are interspersed then the apparent leach rate will go up and down accordingly if the incremental leach rates are plotted as a function of cumulative time.

Although it may be overly simplified, it is worthwhile to look at what a leach curve would be expected to look like for various dissolution curves. Figure 2 has four dissolution curves plotted on it; varying from a very slowly dissolving substance (D) to a substance that reaches saturation almost immediately (A), with two intermediate curves taking 60 (B) and 600 days (C), respectively, to reach saturation. The latter two curves have an arbitrarily drawn rapid first step in the dissolution.

Incremental leach rates calculated from these curves by use of the previous equations are plotted in Fig. 3. The leach rate curves are expanded by plotting the results on a log leach rate versus log (t_n - (t_n - t_{n-1})/2). It needs to be emphasized that t_n is the duration of the leachant renewal period. t_{n-1} would then be the duration of the next shorter leach period, etc. The subscript notation is not used in the sense of a chronological sequence of events. The two extreme cases, very slow dissolution and rapid saturation, produce different curves. The incremental leach rate for the slow dissolution case is constant because there is only minimal build-up of the feedback term; if the periods were increased indefinitely at some point this curve would begin to fall. The rate for the rapid saturation case appears to decrease continuously as the leach period is increased beyond the short period required for saturation to occur while the actual rate is zero once saturation has been achieved. The intermediate curves produce intermediate results. Such plots are a useful test for saturation or other feed-back effects. The extent of the feedback or saturation effects can be estimated from the difference between a time invariant leach rate and the decreasing leach rate curve found when the leach periods are increased. If there were no feedback or saturation effects the leach rate would not be a function of duration of leach period.

If the incremental leach rates are plotted versus 2tn as suggested in the ISO or "modified" IAEA leach tests a leveling for a particular sampling time should occur. On Fig. 4 are plotted the log leach rates of the saturated solution A versus log $(t_n - (t_n - t_{n-1})/2)$ (from Fig. 3) and log $2t_n$ assuming the IAEA leach sequence is followed. On the log leach rate versus log $2t_n$ a leveling occurs for each sample with the same time interval but the overall leach rate still decreases with time because the intervals are constantly increasing. This leveling for a particular duration of leach time should not be interpreted for more than what it is, namely, a pseudoequilibrium between the sample with its characteristics, and the leachant with its contents, for the duration of leaching involved.

Unfortunately, the plotting of the log of the incremental leach rate versus $2t_n$, or log R_n versus log $2t_n$, is the display method used by many scientists studying the leach rate of spent fuel elements.

A second method of displaying leach data recommended by the IAEA is to plot cumulative fraction leached versus cumulative time.

$$\frac{\Sigma a_n}{A_o} \cdot \frac{F}{V} \quad \text{versus } \Sigma t_n$$

Referring back to Fig. 1, the upper two curves in the figure show the cumulative fraction plotted versus cumulative time in the recommended manner. Note the change in slope at 7-10 days that was caused by the two short time samples after the longer sample. It illustrates that cumulative fraction is very dependent upon the leaching times and sequence of sampling and can therefore also be very misleading. Comparisons can be made from one leach test to another only if the tests are carried out in an identical manner and in some standard sequence. This can be shown in a more detailed manner by plotting the cumulative fraction leached versus cumulative time for the four dissolution curves of Fig. 1. These are plotted in Fig. 5. In addition, a curve C′ is added to C that would result if sevea 1 day samples were taken immediately after the weekly samples and before the monthly samples were continued. This illustrates that for comparison purposes some standard sequence must be adhered to. In essence, you are plotting on the same curve leach experiments run under different flow rates. Since the leachant is renewed for each leaching you are imposing a flow rate on the system and that flow rate is set by the length of each leach period.

The IAEA leach test can be useful but care must be taken in the display of the results so that proper interpretation can be made.

References

1. E. D. Hespe, "Leach Testing of Immobilized Radioactive Waste Solids," At. Energy Rev., 9 (1), 195 (1971).

2. "Draft ISO-Standard: Long-Term Leach Testing of Radioactive Waste Solidification Products," ISO/TC 85/SC 5-N28 (1978).

3. A. E. Norris, "Status Report Concerning Empirical Measurements of Fission Product Release from Nuclear Reactor Spent Fuel," ONWI/Sub/79/E511-0120-11, (1979).

Captions

Fig. 1. Leach Rate and Cumulative Fraction of ^{154}Eu Leached from Spent Fuel Elements

Fig. 2. Hypothetical Dissolution Curves

Fig. 3. Leach Rate Versus $t_n - (t_n - t_{n-1})/2$

Fig. 4. Leach Rate Versus Mean Time and Cumulative Time

Fig. 5. Cumulative Fraction Leacned

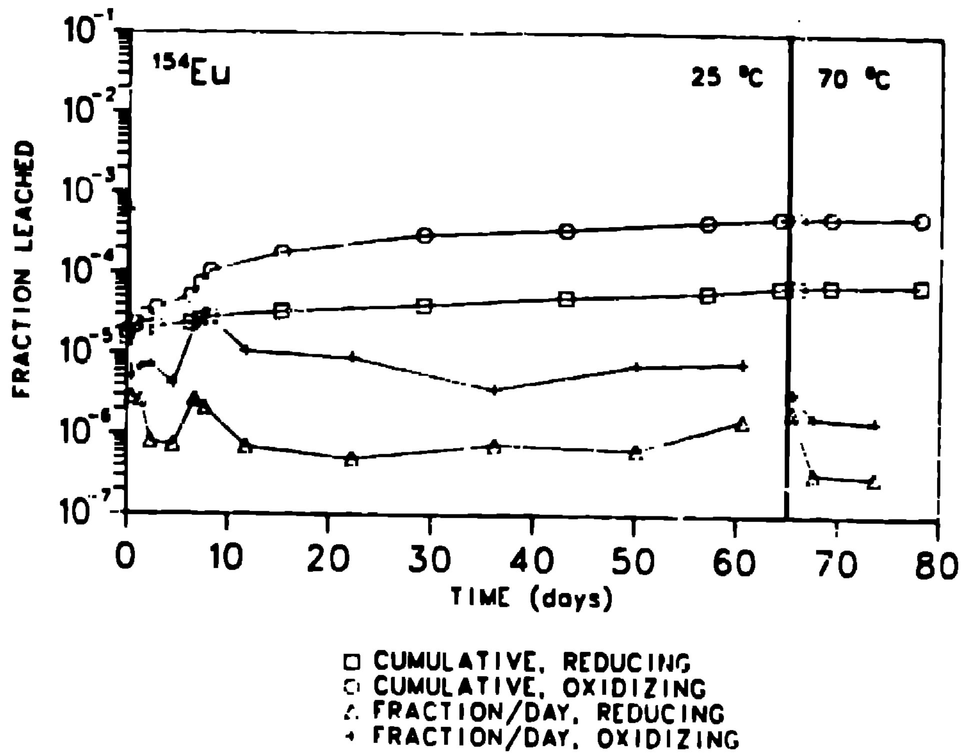

Fig. 1. Leach Rate of Cumulative Fraction of ^{154}Eu Leached from Spent Fuel Elements

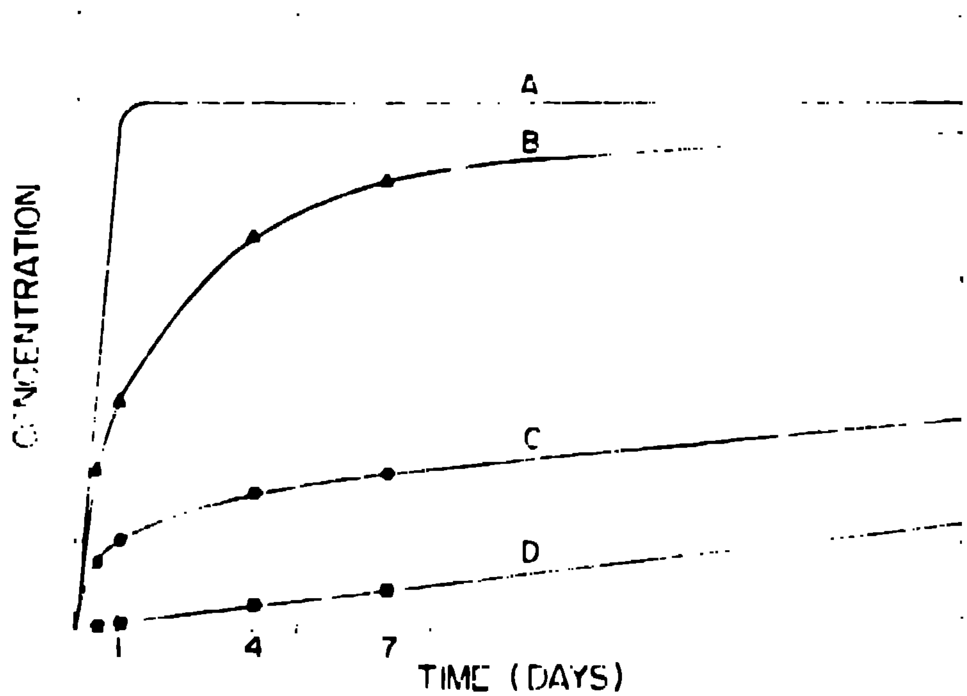

Fig. 2. Hypothetical Dissolution Curves

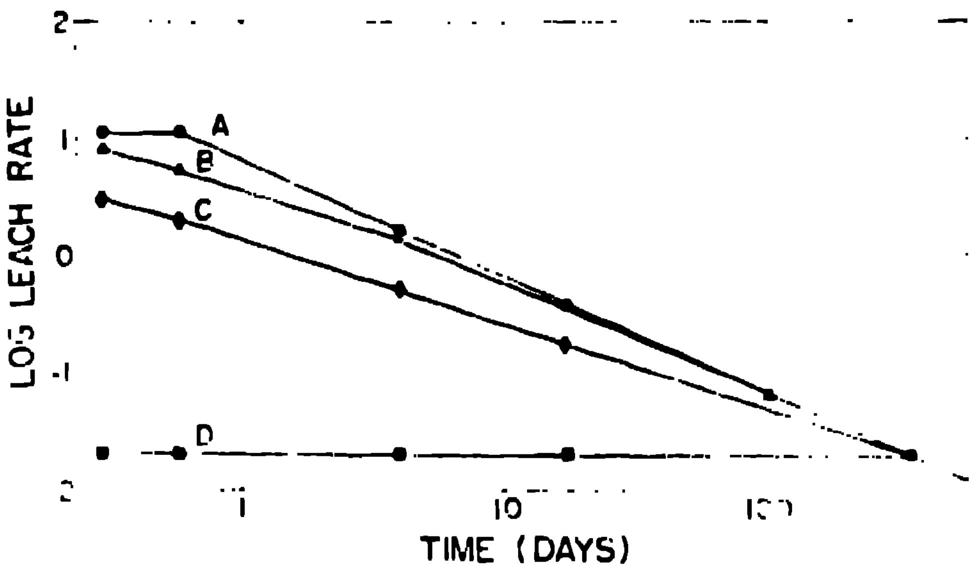

Fig. 3. Leach Rate Versus $t_n = (t_n - t_{n-1})/2$

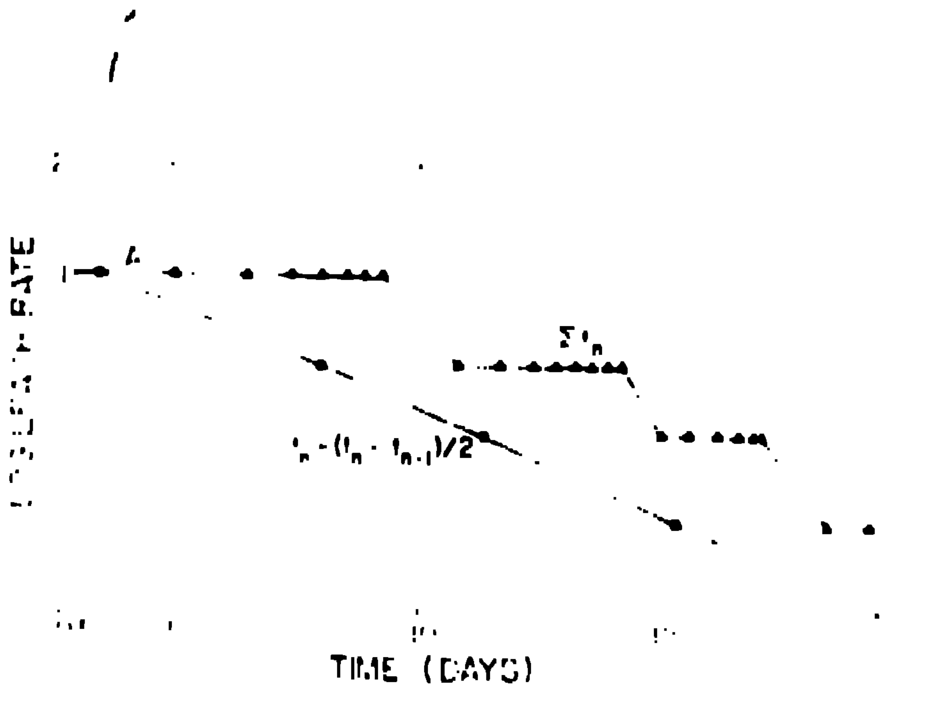

Fig. 4. Leach Rate Versus Mean Time and Cumulative Time

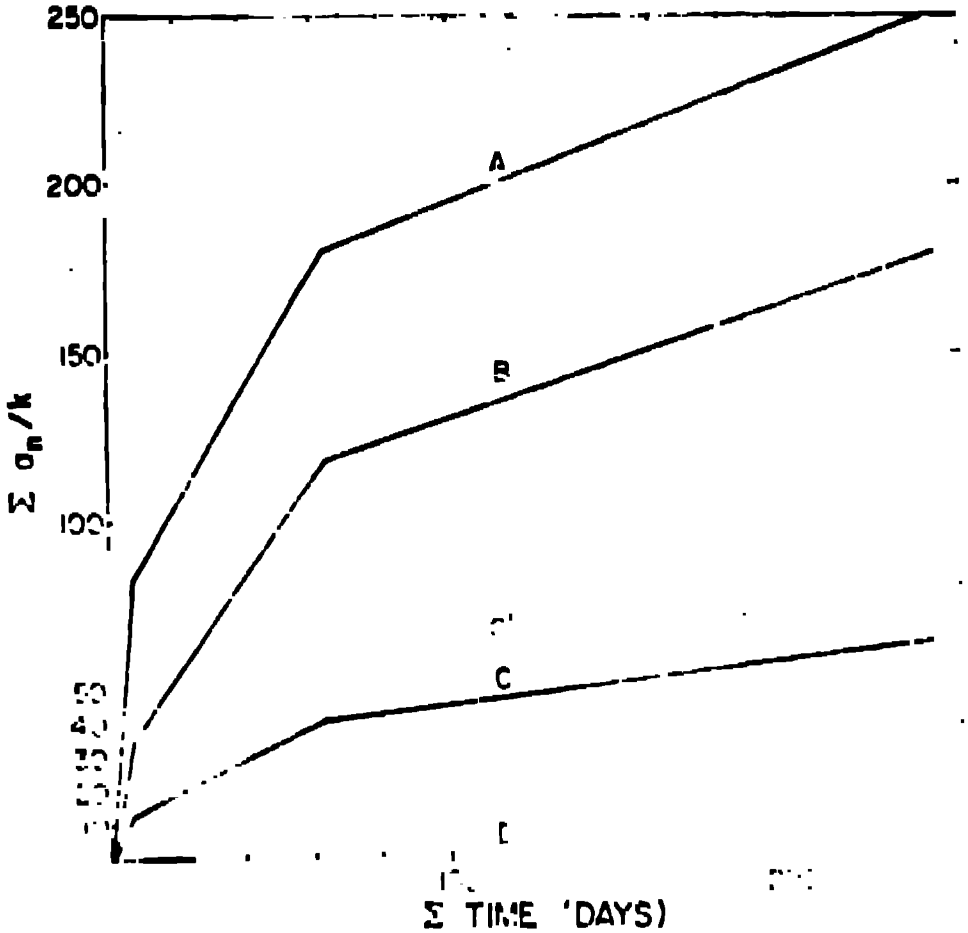

Fig. 5. Cumulative Fraction Leached